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METAL STRUCTURES WITH PARALLEL PORES OF UNIFORM SIZE

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CONTENTS

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ABSTRACT

A wide variety of techniques for preparing metallic structures with parallel, uniformly-sized pores is described critically. One such technique is a commercial process, and at the opposite extreme, others are, perhaps, totally impractical. The method of choice will depend on the characteristics of the structure to be fabricated. Some of the processes described are applicable to materials other than metals.

METAL STRUCTURES WITH PARALLEL PORES OF UNIFORM SIZE

INTRODUCTION

The fabrication of porous metal parts using the techniques of powder metallurgy is an old and well established industry. It is only recently, however, that methods have been developed which make it possible to prepare such structures with parallel pores of uniform size. One company (Reference 1) has made these parallel pore materials available on a semi-commercial basis for experimental and evaluation purposes. Even though there is at present no large volume commercial use for such structures, there is widespread interest in them and numerous potential applications have been proposed. Indeed, these materials have been described as a "solution in search of a problem".

The field of electrochemistry affords two such potential applications, the plaques of sintered plate cells and the electrodes of certain types of fuel cells. These devices are now fabricated by means of conventional powder metallurgical techniques, and are therefore characterized by a random pore structure. In both of these cited examples, the electrochemical reactions involved take place largely within the pores of the structure. Also, in both cases, the detailed mechanisms of the chemical and physical processes which occur are imperfectly understood. It nonetheless seems logical to assume that there is an optimum pore geometry for any given application, and, that this optimum is not attained by the structures now being used. This line of reasoning can be extended to include the hypothesis that the pores in such a device, if optimized, would be uniform in size and perpendicular to the plane of the electrode. Certainly, such structures would be most useful in making theoretical studies of porous electrodes. Several workers have, in fact, reported researches based on this idea (References 2 and 3).

It was considerations such as these which prompted the author to explore the possibility of fabricating such structures with uniformly sized parallel pores. This paper is a report on that effort. It reviews and evaluates the techniques currently available; it describes several new approaches which are now in the process of development; and it proposes several new fabrication methods which appear to have promise.

The end uses, mentioned previously, place certain limitations on the properties of the structures considered here. For example, the electrodes desired are planer or sheet-like objects with perpendicular pores, and ordinarily, a rectangular outline. The thickness could vary, depending on the applications, from a few hundredths of an inch up to as much as a quarter inch. A relatively

high degree of porosity is ordinarily required, perhaps 50 to 90%. The optimum pore diameter for some applications might be as large as 4×10^{-3} inch (100 μm) and for others as small as 4×10^{-6} inch (0.1 μm). Nickel is the preferred material of construction for most of the uses contemplated, but the techniques described are applicable to a broad spectrum of metals, alloys, and other materials.

The various methods of fabrication to be discussed fall conveniently into five categories, including one catch-all or "miscellaneous" group. The other four have been assigned essentially trivial names such as "Elongate-Stack" for ease of reference.

FABRICATION TECHNIQUES

The Elongate-Stack Approach

The first approach to be considered is the only one that has been reduced to commercial practice. At least two companies (References 1 and 4) are using this technique to fabricate metal structures with uniform parallel pores. The details of the process have not been published but the basic idea can be grasped by means of the following example.

The starting material is a copper rod which has been clad with a thick-walled nickel tube. The latter is then machined to obtain a billet having a square cross section. This billet is elongated by a factor of 81, cut into 81 equal lengths, and then reassembled into a 9 by 9 array to form a new billet approximating the original size but containing 81 copper rods, each 1/9th its original size. This process can be repeated one or more times to obtain the necessary reduction in the size of the copper. The billet is then cut into slices perpendicular to the axes of the imbedded copper rods and desired structures are obtained by leaching the copper out of these slices. The minimum size pore that can be obtained by this technique is limited by the interdiffusion of the two metals and by the ability of the leaching solution to penetrate a long thin pore. It has been shown (Reference 4) that it is possible to prepare stainless steel structures with pores that are 4 μm (0.00016 inch) in diameter and 100 μm (0.004 inch) long.

This is a flexible process which can be used to produce a variety of structures. For example, this technique can be made to yield a structure like that shown in Figure 1 by introducing two modifications. First, the copper and nickel are interchanged in the starting material, and second, the slices are sintered to a backing sheet before removing the copper. Without such a backing sheet, the structure would, of course, fall apart.

The Wind-and-Sinter Approach

The second approach can be exemplified by the following process. Fine copper wire is first coated with a nickel electrodeposit. This is wound onto a spool and then sintered to form a coherant mass. After removing the winding from the spool, the wire coil is cut perpendicular to the wires to obtain slices of the desired thickness. Finally, the copper is leached out, yielding a structure having the appearance of Figure 2.

In its details this basic procedure is subject to numerous variations and improvements. It can be shown, for example, that the electrodeposition process becomes impractical for fine wires if one considers both the length of wire involved per unit weight of product and the current carrying capacity of the wire. This difficulty can be circumvented by electroplating a relatively heavy wire and drawing the composite. Even better, one could start by cladding a copper rod with a nickel tube and drawing this structure to the required diameter. Nickel coated copper wire made by the latter process is commercially available (Reference 5).

In some applications a modification of the above process might offer advantages. Instead of starting with nickel coated copper wire, a three-layer structure could be used consisting of an inner copper core, a nickel overlay, plus a second overlay of copper. This could be wound, sintered, and sliced as before. The slices are then sintered or brazed to a nickel backing sheet. As a final step the copper is leached out, leaving a structure with the configuration illustrated in Figure 3. It would, of course, be possible to cover both sides of the backing sheet instead of only one. The basic idea behind this modification is not unlike the one suggested under the Elongate-Stack approach.

W. Kuhn has patented a process for fabricating small-diameter metal capillaries (Reference 6). This product could act as a starting material for the Wind and Sinter approach. The process Kuhn describes is quite flexible but can be explained by the following specific example. A slurry containing a metal powder and a volatile liquid is used to coat a filament made of an organic polymer. The coated filament is then heated in such a way as to decompose and volatilize the filament while sintering the powder into a porous tube. This patent also covers the use of carbon or glass as a filamentary material. The former could be burned away and the latter could be removed by leaching. If used to prepare a nickel structure with parallel pores, a glass or silica filament would be the preferred starting material because either one of these materials could be removed in a final step by leaching with hydrofluoric acid. Glass and silica are both soluble in this reagent, but nickel is not attacked.

For some applications, this process could be modified advantageously by incorporating a small quantity of a brazing material in with the powdered metal. This strategem would make it possible to effect a large reduction in furnace residence time because the tube-forming process would involve melting—which can be very rapid—rather than sintering—which is inherantly slow. The braze could be removed at a later stage in the processing if a porous capillary wall is desired. Cadmium, for example, if used as a braze, could be evaporated. Other brazing materials could possibly be leached.

The sintering step in the Wind and Sinter approach can be replaced with other techniques for consolidating the winding. Recent interest in fiber-metal composites has led to the investigation of a variety of methods for depositing a metal on a spool or mandrel as it is wound with a filament (Reference 7). Withers and Abrams (Reference 8), for example, have demonstrated the feasibility of an electroforming process. They wound the mandrel with a filament while it acted as the cathode in a metal plating bath. By suitable adjustment of such variables as the rates of winding and of electrodeposition, they were able to produce void-free composite structures.

There are several weaknesses in the Wind and Sinter approach. One serious limitation is the cost of fine wire. One alloy investigated, for example, was priced as shown in the following table:

Diameter in Inches	Cost per Pound
0.010	$12.36
0.004	$19.11
0.001	$262.00
0.0005	$1,176.00
0.0004	$4,500.00

Materials such as fused silica, glass, carbon, and various synthetic textile fibers are available in sizes down to about 0.0004 inch (10 μm) and are comparatively inexpensive. It can be seen that the cost factor greatly increases the attractiveness of processes such as slurry coating and electroforming because these can both be adapted to the use of less expensive materials.

The product obtained from the Wind and Sinter approach will not ordinarily conform to the geometrically perfect array illustrated in Figure 2. Such a pattern would result only if the coil winding machine were to perform in a

flawless manner and, to quote a manufacturer of these devices, "....... perfect layer winding is oftentimes an extremely expensive requirement to meet, and one which, under certain circumstances, is virtually unobtainable, regardless of cost" (Reference 9).

As a final objection, it should be noted that axial cuts in a helical coil yield wedge-shaped slices. Slices with parallel sides can be cut, but the process necessarily involves a considerable amount of waste. Eliptical or rectangular spools would probably help, but there seems to be no way to completely circumvent this problem without building a device that would cut and stack straight lengths of fibers. The design of such a device would not be simple.

The Extrude-and-Sinter Approach

The essential aspects of the Extrude and Sinter technique can be pointed out by means of the following example. A heavy slurry or paste is prepared using water, chopped fused quartz fibers, nickel metal powder, a wetting agent, and a thickener or plasticizer. This is forced through a small orifice, thus aligning the quartz fibers into a parallel configuration. The extruded material is cut into convenient lengths, stacked parallel in a suitable container, and compacted while wet to remove entrapped air. The wet compact is fired first at a low temperature to remove water and organic matter, and then at some higher temperature to sinter the nickel powder.

This technique for aligning fibers was first described by L. Frank and H. Barr (References 10 and 11) who used it to prepare high-strength composites that were devoid of pores. For the present areas of application, however, complete compaction is neither necessary nor desirable. Instead, the billet is partially compacted, sintered to increase strength, and then cut into slices with the quartz fibers perpendicular to the plane of the slice. Figure 4 is a photomicrograph of the surface of such a slice. The cut ends of the half-mil (10 μm) quartz fibers appear as black disks. The lighter background is sintered nickel powder having a porosity of about 30 percent. The desired structure with parallel pores is obtained by dissolving the quartz in hydrofluoric acid.

The feasibility of this approach has been demonstrated in investigation which is currently in progress (Reference 12). The details of this project will be reported separately.

It should be noted that this fabrication process yields a structure having two kinds of pores; induced pores caused by the removal of the quartz filaments, and interstitial pores resulting from the incomplete compaction of the powder-metal matrix. Also, the amount of porosity from each source can be controlled and the diameter of the induced pores is essentially uniform. This dual porosity

is also characteristic of the slurry coating variations of the Wind and Sinter approach previously described.

The details of the fabrication process and the nature of the materials used in the Extrude and Sinter approach can both be varied to meet the needs of a specific end product. The basic process could be used, for example, to produce sieves having holes smaller than any practical sieve currently available. Here, it would be necessary to have essentially straight induced pores with smooth walls. Otherwise, clogging of these pores would almost certainly be a problem. Such straight smooth induced pores could be obtained by avoiding mechanical compaction and, instead, filling the interstitial pores with a braze prior to removal of the pore-former.

In some applications it would be desirable to reduce the diameter of the induced pores to a micro meter or less. The fuel cell electrode is perhaps a case in point. All of the potential pore-formers investigated, glass, quartz, metal wire, and the various synthetic organic fibers, are available in diameters as small as five to ten micrometers, but it seems that not one of these materials is available in a size range less than this.

This dilemma could perhaps be resolved by combining the Elongate-Stack and the Extrude and Sinter approaches. Thus, one could start with 0.004 inch (100 μm) copper wire as a pore former. This comparatively inexpensive and easy to handle. Using the Extrude and Sinter approach, this wire could be dispersed as short parallel segments in, for example, a nickel billet. The Elongate-Stack approach could then be used to effect two consecutive ten-fold reductions in the billet cross section, thus reducing the diameter of the copper wires from 100 to one micrometers. The final steps would involve slicing and leaching as previously outlined.

A number of interesting possibilities are raised if one introduces the idea of coating the pore-former (wire, glass filament, etc.) before using it in the Extrude and Sinter approach. For example, copper wire coated with a platinum electrodeposit could be used to fabricate a nickel fuel cell electrode with platinum-lined pores. This coating technique would be beneficial if the end product were to be a sieve. Thus, if one coated silica fibers with nickel metal before using this composite to prepare a nickel sieve, one could be assured that the largest hole diameter would be the same as the largest quartz filament because the clumping of two or more filaments would not cause the formation of an over-size pore.

Finally, it should be noted that the Extrude and Sinter approach is applicable to materials other than metals. Ceramics and plastics are likely candidates.

The Corrugate-Stack Approach

The Corrugate-Stack approach was first proposed by J. McCallum (Reference 2) as a potential technique for fabricating plaques for the nickel cadmium cell. Like the Extrude and Sinter approach, it is the basis for a current investigation (Reference 13), the details of which will be reported separately. This paper will discuss only the basic idea and a few of the more significant findings.

In its essence, the procedure is as follows. Corrugated metal sheets are formed and then stacked with the grooves of all the sheets running parallel. This assembly is sintered to form a coherant mass and then sliced in a direction such that the plane of the slice is perpendicular to the grooves formed by the corrugations. The slices thus obtained are the desired parallel-pore structures.

Present indications suggest that this is a thoroughly practical process, but it is not without its difficulties and limitations. One problem which is immediately apparent is the fabrication of sheets with both a metal thickness and a corrugation depth in the order of a thousandth-of-an-inch. This has been solved by means of an electroforming technique, but the handling of this material in the absence of special machinery is a tedious hand process. It can be seen that the need for a high degree of porosity, e.g., 70-80 percent, constrains any effort to minimize this difficulty. Present indications are that the Corrugate-Stack approach is not a practical route to pore sizes less than a thousandth-of-an-inch.

A second difficulty is the tendency of adjacent sheets to nest, thus obliterating the pores. What seems to be an effective solution to this problem is illustrated in Figure 5, which illustrates that the use of alternate layers of uncorrugated sheet prevents such nesting. Also, note that the corrugations in any given sheet make an angle of about 30 degrees with those in the corrugated sheets immediately above and below. This angling of the corrugations with respect to those above and below increases the compressive strength of the assembly. With parallel corrugations these structures tend to be distorted as shown in Figure 6 when subjected to a compressive stress during sintering.

Experience with slicing this type material is limited but it seems probable that it will be necessary to fill the voids with wax or some similar substance before cutting. This could be removed subsequently by melting and/or solvent extraction.

Figure 7 is a photomicrograph of a finished structure. The peak-to-peak distance of the corrugations in this structure is 10 mils (250 μm).

Miscellaneous Approaches

This category of fabrication techniques includes all those approaches which seem to have less merit in present applications than those previously described. They are included here for the sake of completeness and because these methods might take on a greatly enhanced attractiveness to the reader with a different end-use in mind.

The Stacked-Screens Approach. McCallum, et. al. (Reference 2) have investigated a fabrication technique based on the use of stacked electroformed screens. The fine-mesh screens required are available commercially (Reference 14) or they can be prepared using conventional electroforming or photoengraving techniques. The interested reader is referred to the references just cited, or to the manufacturers of the photoresist materials which are commonly used in an essential step in these processes.

These techniques for preparing screens can not be modified to yield porous bodies of the type under consideration here, i.e., relatively thick structures with long, thin pores. McCallum circumvented this problem by superimposing one screen on another until the required thickness, or pore length, was attained. This was done while maintaining alignment or registration of all the layers involved. In this way, an assembly with straight pores was obtained. The apparatus developed to accomplish this was mounted on the stage of the microscope used to observe the position of each succeeding layer. After being so assembled, the mass was sintered to form a coherant body.

It is obvious that this technique, even though it is both ingenious and effective, is not suited to the production of parallel pore structures in any quantity greater than that needed for small scale laboratory experiments.

The Flock Approach. The word "flock" is used to describe a process in which short lengths of textile fibers are dropped onto an adhesive-coated surface to obtain a matte or felt-like finish. In a refinement of this technique, the fibers are dropped through an electrostatic field, thus aligning them perpendicular to the surface. The velvet finish usually applied to jewelry boxes, for example, is obtained in this way.

One can conceive of this process being duplicated using metal in place of fabric, thus producing a structure like that shown in Figure 1. The feasibility of this technique was explored in a rather crude series of experiments, by dropping short lengths of fine nickel wire through a magnetic field generated by a solenoid. These experiments were inconclusive but at least one problem was encountered, a tendency of the "fibers" to clump and other problems were

anticipated. None of these problems seem to be insurmountable, but the flocking of metals must nonetheless be viewed at the present time as an interesting but unproven technique.

The Weaving Approach. Metal wire cloth is commercially available in a wide variety of weave patterns, metals, wire sizes, etc. It is obvious that by stacking and sintering some of these could be used to prepare structures which would be described as having parallel pores. A more sophisticated, but similar, approach would replace the conventional loom with a computer-controlled filament-winding machine of the type that has been developed to form fiber-reinforced composites. Any such weaving process, if used to prepare structures of the type contemplated here, is subject to criticism on at least two counts, the cost of the wire and the enormous lengths that would be required per unit weight of product. A pound of one mil nickel wire, for example, is sixty miles long. The strength of such wire might also present a formidable problem. It is clear that the various weaving processes are not very practical when viewed in the light of present requirements.

The Metallized-Velvet Approach. Pile-type fabrics such as velvet and the oriented flock-type material just mentioned are available in great variety, and are relatively inexpensive. Bauman (Reference 15) has suggested that these materials could be metallized to obtain a parallel-pore structure by using the parallel fibers of the nap as a pore-former. The practicality of this general approach has been demonstrated by Botosan and Katan (Reference 16) who metallized a felt-type fabric and then tested it as a fuel cell electrode. Justi (Reference 17) has investigated a somewhat similar method, which also uses a pile-type fabric as a pore-former. He fills the voids in the fabric with metal powder, which is subsequently consolidated by mechanical compaction and/or sintering. The fabric skeleton can be either burned off or left in place depending on both the metal involved and the particular application.

This technique has several obvious limitations, and is certainly less versatile than others discussed above. It would perhaps be attractive in some special applications.

The Alginate Honeycomb Approach. H. Thiele and A. Wiechen have described an interesting process based on the replication of alginate film (Reference 18). By means of appropriate chemical processing, (Reference 19) such films can be prepared with pores that are normal to the film surface, essentially identical in diameter, and with a remarkably uniform distribution over the face of the film. It is claimed that pore size and degree of porosity can both be controlled and varied over a wide range.

After they have been strengthened by a rather complex process involving both dehydration and plastic impregnation, these films can be metallized to

obtain a similar structure in, for example, nickel. The organic skeleton can then be removed, if necessary, by a process such as pyrolysis or leaching.

It is difficult to evaluate the practicality of this approach without first-hand experience with the processes involved. The references cited indicate that the steps are numerous but easily controlled and subject to automation. Certainly, it offers at least one significant advantage over most of the approaches previously described, in that, there is no slicing step. If the structure required is relatively thin but large in area, this step can be very wasteful and difficult, or even totally impractical. The Alginate Honeycomb approach obviates this limitation and places no practical limitation on the area. In short, this is an attractive approach which should be evaluated by anyone interested in parallel pore structures.

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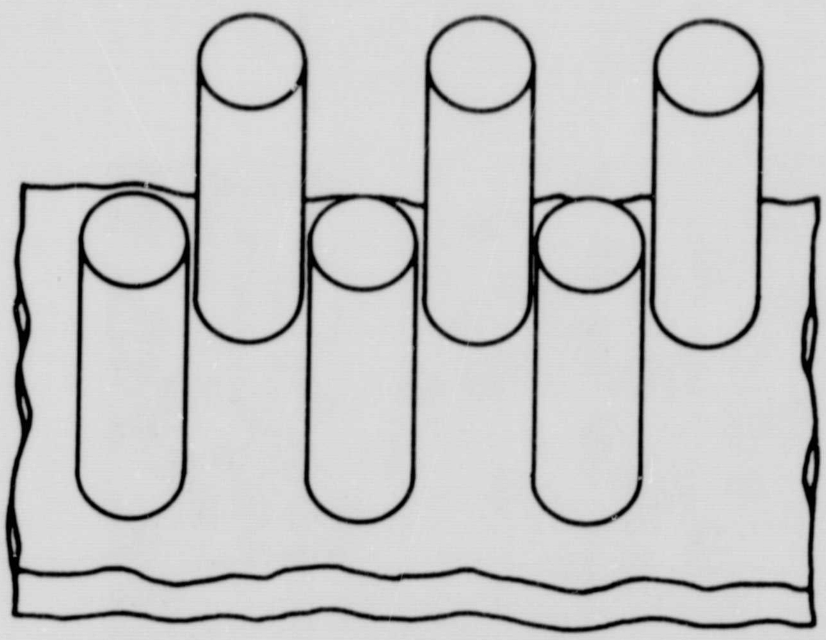

Figure 1

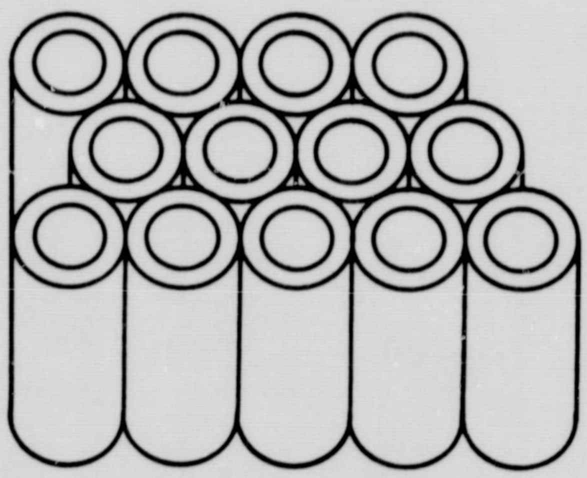

Figure 2

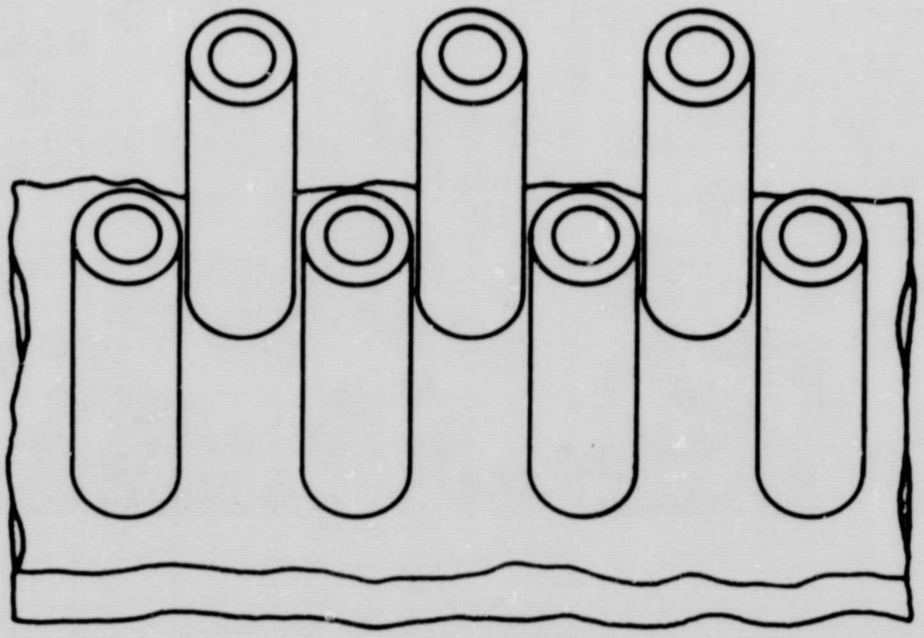

Figure 3

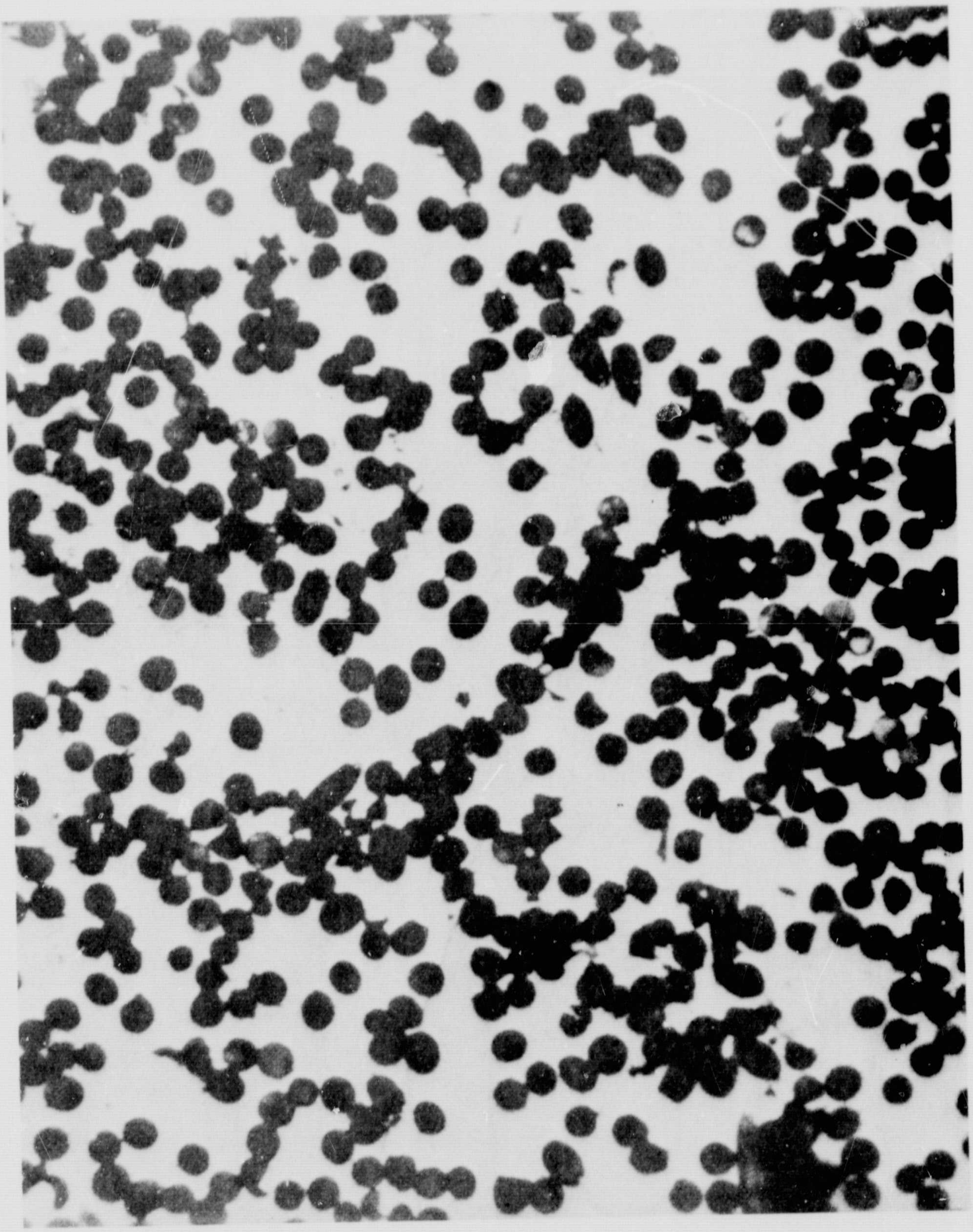

Figure 4

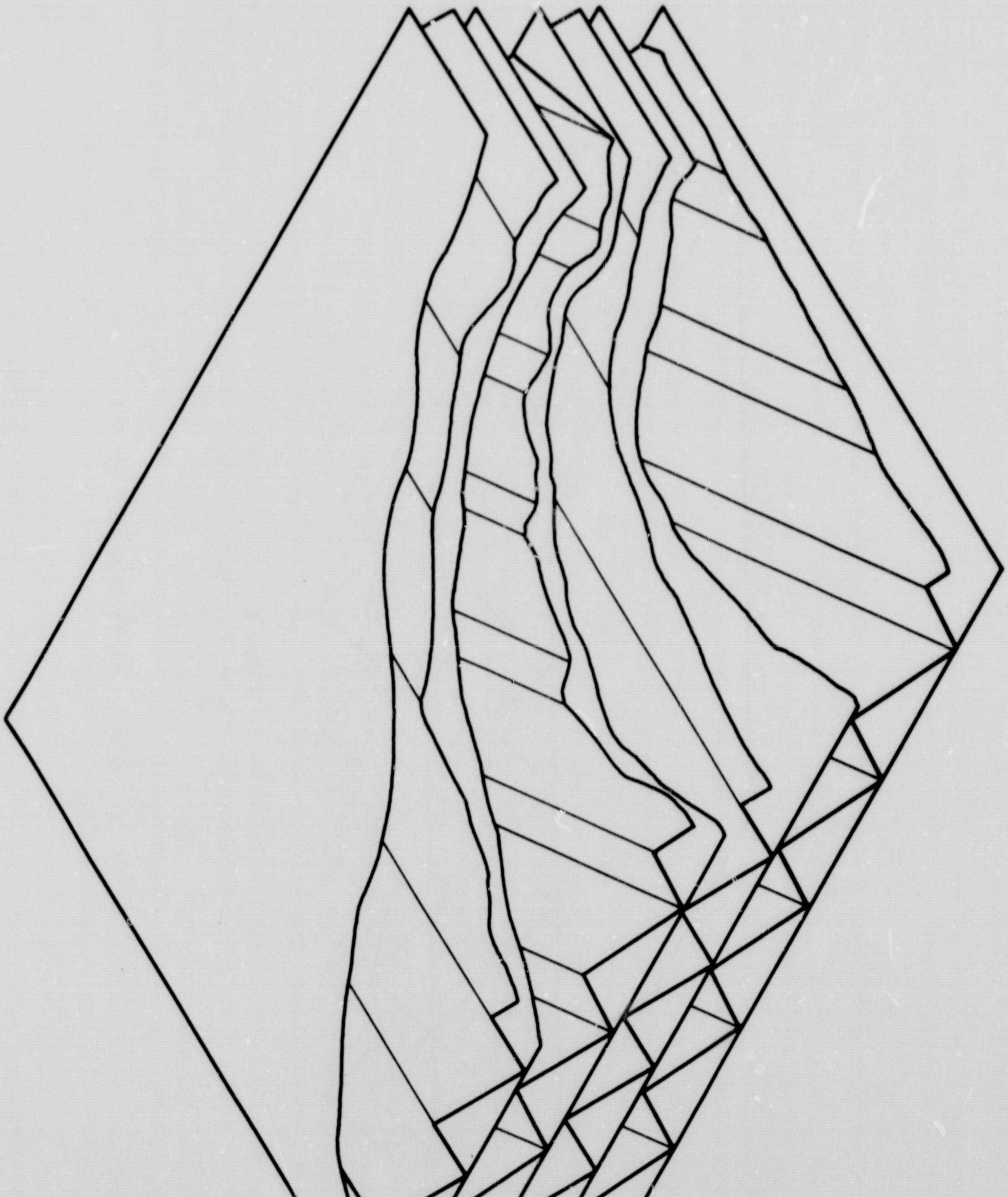

Figure 5

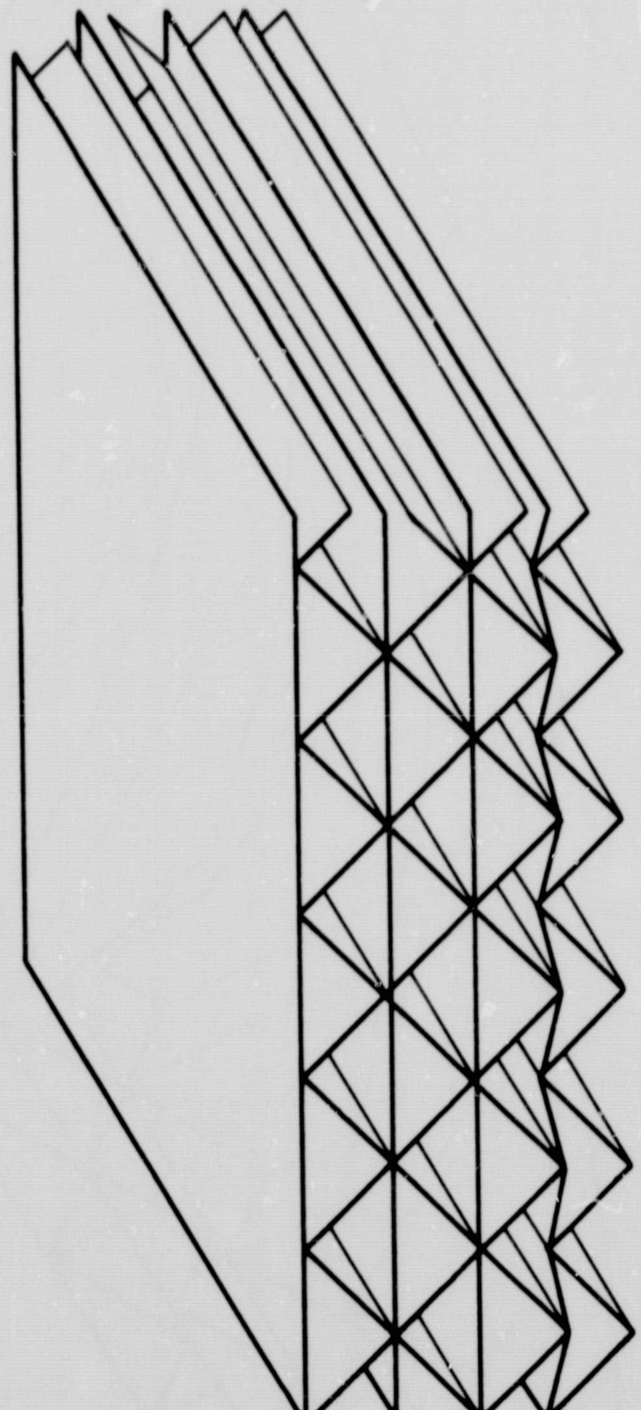

Figure 6

Figure 7